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Alkene and thioether oxidations with H_2O_2 over Ti-containing mesoporous mesophase catalysts

Oxana A. Kholdeeva [a,*], Alexander Yu. Derevyankin [a], Alexander N. Shmakov [a],
Nataliya N. Trukhan [b], Eugenii A. Paukshtis [a], Alain Tuel [c],
Vyacheslav N. Romannikov [a,1]

[a] *Boreskov Institute of Catalysis, 5 Acad. Lavrentiev Avenue, Novosibirsk 630090, Russia*
[b] *Novosibirsk State University, Novosibirsk 630090, Russia*
[c] *Institut de Recherches sur la Catalyse, C.N.R.S., 2 Avenue Albert Einstein, 69626 Villeurbanne Cedex, France*

Abstract

Well-organized Ti-containing mesoporous mesophase materials (Ti-MMM) have been synthesized by hydrothermal synthesis using $C_{16}H_{33}N(CH_3)_3Br$ and characterized by elemental analysis, IR, DRS-UV, XRD, and N_2 adsorption. Catalytic properties of these materials in alkene and thioether oxidations with aqueous H_2O_2 in CH_3CN have been studied and compared with those of the Ti-containing hexagonal mesoporous silica (Ti-HMS). The Ti-MMM catalysts with the Si/Ti atomic ratio varying in the range of 49–124 showed the highest catalytic activities in alkene oxidation. Both the structure of a silicate matrix and a degree of isolation of titanium ions in it are crucial factors determining catalytic activity of Ti-MMM. For thioether oxidation, the structural perfection of Ti-MMM catalysts is less important. No leaching of titanium ions occurs during both reactions. The oxidation process proved to be truly heterogeneous. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Titanium; Mesoporous mesophase catalysts; Oxidation

1. Introduction

Selective catalytic oxidations attract much attention due to the versatility of oxygen-containing compounds in organic synthesis. Mesoporous mesophase materials (MMM), containing transition metal ions highly dispersed in a regular silicate matrix, due to the proper pore size and high surface area are of great interest for oxidation of large organic molecules [1–5]. Here, we report on the structural and catalytic properties of Ti-MMM prepared using $C_{16}H_{33}N(CH_3)_3Br$ by hydrothermal synthesis in alkene and thioether oxidation with aqueous H_2O_2 and compare them with structural and catalytic properties of another type of mesoporous catalyst — the Ti-containing hexagonal mesoporous silica (Ti-HMS). An attempt was made to distinguish between true heterogeneous catalysis, versus catalysis in homogeneous solution.

* Corresponding author. Tel.: +7-383-2-344573; fax: +7-383-2-343766.

E-mail addresses: khold@catalysis.nsk.su (O.A. Kholdeeva), tuel@catalyse.univ-lyon1.fr (A. Tuel).

[1] Also corresponding author.

2. Experimental

Ti-HMS (sample **1**) was synthesized according to Ref. [1]. Ti-MMM (samples **2–5**) and SiO$_2$-MMM (sample **6**) were prepared in the presence of C$_{16}$H$_{33}$N(CH$_3$)$_3$Br by hydrothermal synthesis at 140°C followed by the surfactant removal by calcination in air flow at 550–600°C. All the calcined catalysts were characterized by elemental analysis, IR spectroscopy of CO adsorbed at ∼ 77 K, DRS-UV, XRD using synchrotron radiation, and the N$_2$ adsorption measurements. Textural parameters were calculated as described in Ref. [6]. Oxidation experiments were carried out in thermostated glass vessels (50 and 20°C for oxidation of alkenes and thioethers, respectively) under vigorous stirring. The reaction was initiated by adding 0.33 mmol of 35% aqueous H$_2$O$_2$ to a MeCN solution (3 ml) containing 0.30 mmol of an organic substrate, 6–60 mg of a catalyst (0.006 mmol of Ti) and an internal standard. The oxidation products were identified by GC-MS and ^{1}H NMR and quantified by GC. H$_2$O$_2$ conversion was determined by iodometric titration. After the reaction catalysts were filtrated, they were washed with acetone and water, dried, calcined in air at 540°C for 4 h and then re-used.

3. Results and discussion

The XRD patterns of the calcined Ti-MMM studied (samples **3–5**, Fig. 1) are of well-known overall type [3,5] and very similar to that of pure siliceous MMM (samples **6**). Unlike most earlier published data [1–3,5], the reflections observed in this work are of Gaussian shape with the full-width-at-half-maximum (FWHM) values about 0.07–0.09° 2θ (Table 1). The peculiarities of the XRD patterns allow us to describe the structure of samples **3–5** as highly-ordered hexagonal arrangement of mesopores, which is indirectly supported also by a narrow interval of relative pressure $\Delta(P/P_0)$, within which the nitrogen capillary condensation occurs during low-temperature adsorption (Fig. 2), along with relatively small values of the external surface area (Table 1), calculated from the comparative graphs as described in Ref. [6]. If the Ti content in the Ti-MMM is increased (sample **2**), or the method of preparation is changed (sample **1**), a decrease of structure perfection can be clearly seen (Figs. 1 and 2; Table 1).

DR-UV spectra (Fig. 3) are similar for samples **4** and **5** ($\lambda_{max} = 225$ nm) and, according to Ref. [7], indicate isolated titanium ions. For
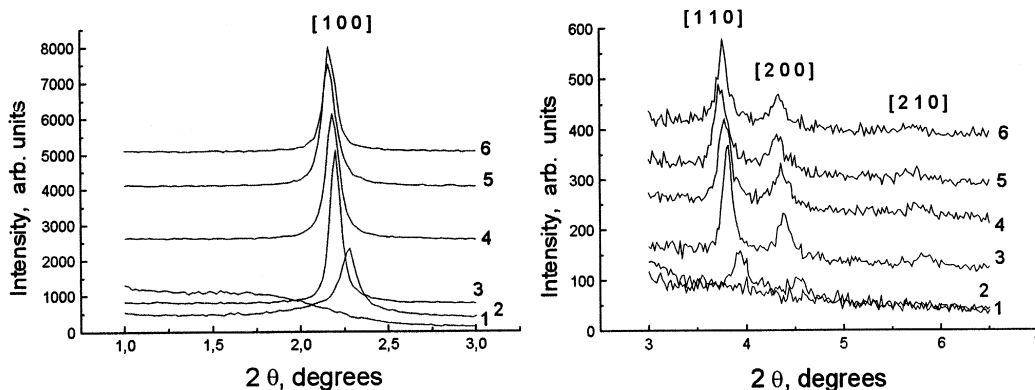

Fig. 1. Two most important angle regions of the XRD patterns of the samples studied. Curve numbers correspond to the sample numbers in Table 1.

Table 1
Structural, textural and catalytic characteristics of Ti-MMM calcined samples

Sample no.	Cyclohexene conversion for 4 h (%)	Si/Ti, (at. ratio)	Structural parameters		Textural parameters			
			a_0^a (nm)	FWHM^b (deg 2θ)	A_{me}^c (m²/g)	A_{ext}^d (m²/g)	V_{me}^e (cm³/g)	$\Delta(P/P_0)^f$
1	28	30	–	> 0.5	627	170	0.887	0.327
2	28	19	4.47	0.117	911	86	0.738	0.071
3	31	49	4.64	0.078	1059	53	0.908	0.064
4	33	124	4.68	0.086	1068	48	0.932	0.062
5	18	166	4.71	0.093	1015	44	0.887	0.064
6	0	$\propto$	4.72	0.071	1065	44	0.930	0.067

[a] Unit cell parameter.
[b] Full-width-at-half-maximum of the [100] reflection.
[c] Specific mesopore surface area.
[d] Specific external surface area.
[e] Specific pore volume.
[f] Pressure interval of the N_2 capillary condensation.

samples **1–3**, the UV absorption maximum shifted to longer wavelengths and the band is broader. This may be most probably due to the presence of partially clustered titanium-oxygen species [8]. The described ideas on the state of titanium ions in the samples studied as well as an interdependence of this state with total titanium content are also supported by IR spectra of adsorbed CO (Fig. 4). Three types of the bands are observed in the spectra: at 2135 cm^{-1} (associated with physically adsorbed CO), at 2153 cm^{-1} (related to the complexes of CO with silanol groups, which are observed at

3730–3740 cm^{-1} in the OH-group region [8]), and at 2179 cm^{-1} (corresponded to the interaction of CO with titanium cations localized outside the silicate matrix [9]). It is also seen in Fig. 4 that the latter complexes are found in the highest concentration in the cases of samples **1** and **2**. For the rest of the samples, the intensities of the bands at 2179 cm^{-1} diminish with decreasing Ti content.

The activities of the Ti-MMM samples in alkene oxidation were compared using cyclohexene as a model substrate and were found to fall in the order: **4 > 3 > 1, 2 > 5 ≫ 6** (Table 1). Cyclohexene oxide and the corresponding diol predominated in the oxidation products. Small amounts of allylic oxidation products were
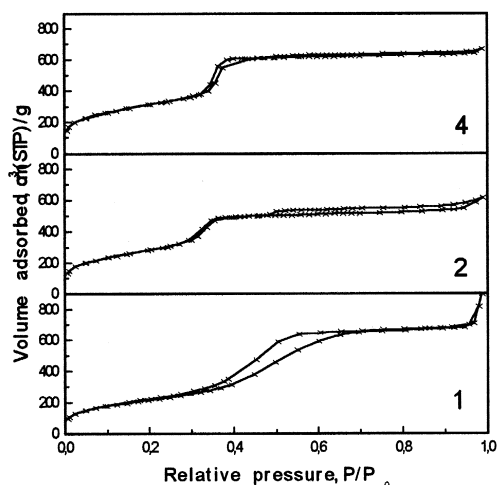

Fig. 2. Nitrogen adsorption isotherms of the samples studied. Curve numbers correspond to the sample numbers in Table 1.
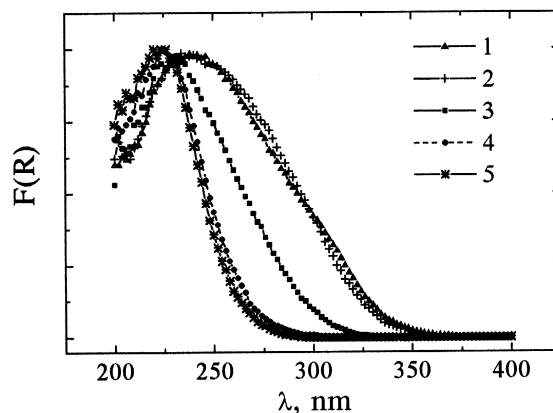

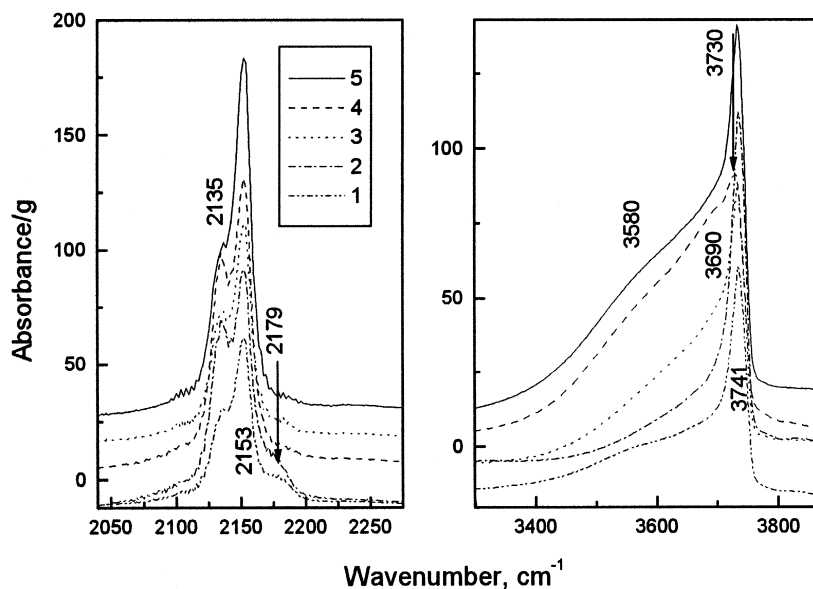Fig. 3. UV–Vis diffuse reflectance spectra for the samples **1–5**.

Fig. 4. IR spectra of adsorbed CO (left) and of the OH group region (right) for the samples studied. Curve numbers correspond to the sample numbers in Table 1.

also detected by GC-MS. Yields of cyclohexene oxidation products based on H_2O_2 consumed are moderate (38–45%) since nonproductive peroxide decomposition occurs significantly. When more nucleophylic alkene, ($-$)-caryophyllene was used, the efficiency of H_2O_2 utilization was rather high: selectivity of epoxidation attained 72%, 4,5-monoepoxide being the main product. Note that both substrates, especially caryophyllene, are too large to be successfully oxidized using microporous Ti-silicalites, such as TS-1 or TS-2 [10]. We have found that the well-organized Ti-MMM catalysts with

the Si/Ti ratio in the range of 49–124 showed the highest catalytic activities in cyclohexene oxidation. The lower activity of sample **5**, in spite of isolated state of titanium ions in it according to DR-UV and IR data (Figs. 3 and 4), was probably caused by its more substantial destruction in the presence of water as compared with sample **4**, as was observed earlier for pure SiO_2-MMM [11].

By contrast to cyclohexene oxidation, all the samples studied showed similar activity and selectivity, independently of their structural and textural properties as well as the titanium state,

Table 2
Methyl phenyl sulfide (MPS) oxidation with H_2O_2 over sample **4**

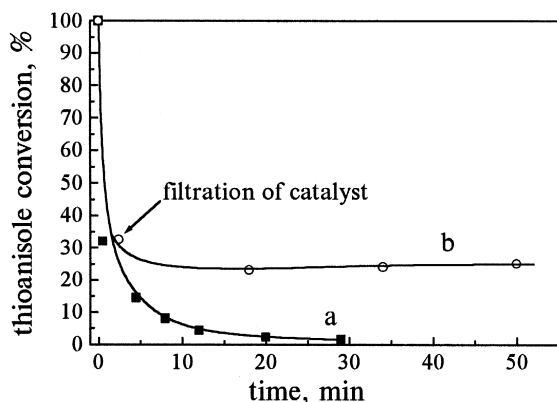|	Ti (wt.%)	MPS conversion in 20 min (%)	Product distribution	
			Sulfoxide (%)	Sulfone (%)
Before reaction	0.58	–		
I cycle	0.61	95	76	24
II cycle	0.57	84	77	23
III cycle	0.62	74	76	24

Fig. 5. Thioanisole conversion vs. time: (a) over sample **4**; (b) in filtrate after fast removal of the catalyst.

in thioether oxidation, which proceeded efficiently at room temperature to yield the corresponding sulfoxide and sulfone. Thioanisole conversion was 94–98% in 20 min for all the catalysts, sulfoxide/sulfone ratio being 76:24. Note that the Ti-MCM-41 catalysts showed less activities in this reaction [12]. Particular attention was devoted to the question of leaching of titanium ions during the reaction. According to elemental analysis data, titanium content did not decrease after three catalytic cycles (Table 2). Substantial titanium leaching, which was observed recently in Ref. [13], was probably due to the employment of MeOH and high H_2O_2 concentrations. Additionally, we have found that after fast filtration of the reaction mixture the reaction does not proceed in the filtrate, which was colorless (Fig. 5). Similar behaviour was observed for caryophyllene oxidation. This confirms that both alkene and thioether oxidations with H_2O_2 over Ti-MMM catalysts are true heterogeneous reactions. Therefore, some decrease in the Ti-MMM catalytic activity observed after recycling (Table 2) is not a result of titanium leaching. We believe that this decrease arises from the loss of the regular mesoporous structure during the regeneration process as it was observed for aluminosilicate MMM with relatively low aluminium concentration [14].

4. Conclusion

The present study demonstrates that both the structure of a sample and the high dispersion of titanium in it are crucial factors determining catalytic behavior of Ti-MMM in alkene oxidation, whereas for thioether oxidation the structural perfection of Ti-MMM is less important. No leaching of titanium occurs during both reactions. The oxidation process appeared to proceed in the heterogeneous matrix.

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